

09/853, 314

O P I C
OFFICE DE LA PROPRIÉTÉ
INTELLECTUELLE DU CANADA



C I P O
CANADIAN INTELLECTUAL
PROPERTY OFFICE

(12) (19) (CA) **Demande-Application**

(21) (A1) **2,211,200**

(86) 1996/01/10

(87) 1996/08/01

(72) CREMER, Jürgen, DE

(72) KOCUR, Jean, DE

(72) KRUG, Georges, DE

(71) HOECHST SCHERING AGREVO GMBH, DE

(51) Int. Cl.⁶ A01N 57/20

(30) 1995/01/24 (195 01 986.5) DE

(54) **AGENTS HERBICIDES SYNERGIQUES A BASE DE
GLUFOSINATES ET D'ETHERS DE NITRODIPHENYLE ET
LEURS FORMULATIONS**

(54) **SYNERGISTIC HERBICIDAL COMPOSITIONS BASED ON
GLUFOSINATE AND NITRODIPHENYL ETHERS, AND
THEIR FORMULATIONS**

(57) L'invention concerne des agents herbicides contenant A) des glufosinates ou leurs sels ou bien des agents analogues comme le bialaphos, B) un herbicide aux éthers de nitrodiphényle comme l'oxyfluorophène et C) un tensioactif d'alkylpolyglycoléthersulfate. Ces agents herbicides présentent des effets herbicides synergiques. Les constituants A, B et C peuvent être formulés conjointement sous forme d'une émulsion aqueuse dans laquelle il y a 1-15 % de A, 0,1 à 5 % de B, 1-15 % de C, 3 à 30 % de solvant organique, 40-60 % d'eau, 2-10% d'émulsifiant et 0 à 20 % d'adjuvants de formulation usuels.

(57) Herbicidal agents containing A) glufosinates or their salts or similar agents like bialaphos, B) a nitrodiphenyl ether herbicide like oxyfluorophene and C) an alkyl polyglycol ether sulphate tenside have synergistic herbicidal effects. Components A, B and C can be jointly formulated in the form of an aqueous emulsion in which there are 1-15 % A), 0.1 to 5 % B), 1-15 % C), 3 to 30 % organic solvent, 40-60 % water, 2-10 % emulsifier and 0 to 20 % ordinary formulation auxiliaries.



Industrie Canada Industry Canada

WO 96/22692

- 1 -

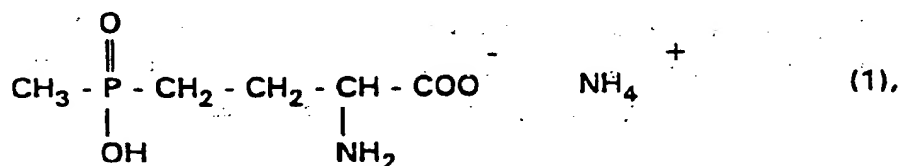
PCT/EP96/00072

Description

Synergistic herbicidal compositions based on glufosinate and nitrodiphenyl ethers, and their formulations

The invention is in the field of the crop protection products which can be employed against undesirable vegetation, in particular of combinations of herbicides.

Glufosinate-ammonium (phosphinothricin-ammonium) (1)



i.e. the ammonium salt of 4-[hydroxy(methyl)phosphinoyl]-DL-homoalanine, is a known herbicide which is taken up via the green parts of the plant (foliar-acting herbicide); see "The Pesticide Manual" 9th Edition, British Crop Protection Council 1991, p. 458. Glufosinate-ammonium is mainly employed post-emergence for controlling broad-leaved weeds and grass weeds in plantation crops and on uncultivated land and, by means of specific application techniques, also for inter-row treatment in agricultural row crops such as maize, cotton and the like. The compound of the formula (1) contains an asymmetric carbon atom. The L-enantiomer is considered to be the biologically active isomer.

It has furthermore been disclosed that the action of glufosinate-ammonium and the action of its L-enantiomer can be markedly improved by surfactants, preferably by wetting agents from the series of the alkyl polyglycol ether sulfates, which are used, for example, in the form of their alkali metal salts or ammonium salts, but also as the magnesium salt, such as sodium C₁₂/C₁₄-fatty alcohol

- 2 -

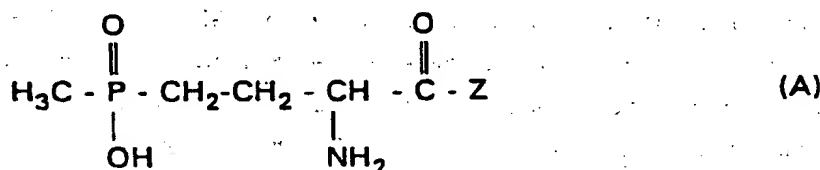
diglycol ether sulfate ([®]Genapol LRO, Hoechst); see EP-A-0476555, EP-A-0048436, EP-A-0336151 or US-A-4,400,196, and Proc. EWRS Symp. "Factors Affecting Herbicidal Activity and Selectivity", 227 - 232 (1988).

- 5 It has furthermore been disclosed that alkyl polyglycol ether sulfates are also suitable as penetrants and synergists for a series of other herbicides, inter alia also for diphenyl ether herbicides; see EP-A-0476555.

10 Surprisingly, it has now been found that glufosinate-ammonium or related active substances can advantageously be combined together with certain nitrodiphenyl ether herbicides and anionic surfactants from the series of the alkyl polyglycol ether sulfates as penetrants, resulting in synergistically increased activities.

- 15 The invention therefore relates to herbicidal compositions which comprise an effective content of a combination of

- A) one or more compounds of the formula (A) or salts thereof



20 where

Z is a radical of the formula -OM, -NHCH(CH₃)CONHCH(CH₃)COOM or -NHCH(CH₃)CONHCH[CH₂CH(CH₃)]COOM in which M is in each case hydrogen or an inorganic or organic cation,

25

- B) one or more compounds of the group of the nitrodiphenyl ether herbicides and
C) an anionic surfactant from the series of the alkyl polyglycol ether sulfates.

- 3 -

Formula (A) embraces all stereoisomers and their mixtures, in particular the racemate and the enantiomer which is biologically active in each case.

5 Examples of active substances of the formula (A) are the following:

- a1) glufosinate, which has already been mentioned, and its ammonium salt in racemic form,
- a2) the L-enantiomer of glufosinate and its ammonium salt,
- 10 a3) bialaphos (or bilanafos), i.e. L-2-amino-4-[hydroxy-(methyl)phosphinyl]butanoyl-L-alanyl-L-alanine and its sodium salt.

The racemate of glufosinate-ammonium on its own is conventionally applied at dosages between 200 and 1000 g of a.i./ha (= gram of active ingredient per hectare). At
15 such dosages, glufosinate-ammonium is especially effective when taken up via green parts of the plant. Since it is microbially degraded in the soil within a few days, it has no long-term action whatsoever in the soil. This also
20 applies analogously to the related active substance bialaphos-sodium; see "The Pesticide Manual" 9th Ed. British Crop Protection Council 1991, p. 75.

Examples of dinitrophenyl ether compounds (B) are

- 25 b1) oxyfluorfen, i.e. 2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-trifluoromethylbenzene, whose use as a single active substance at 100 - 1000 g of a.i./ha is known pre- and post-emergence in soya beans, and also on uncultivated land;
- b2) lactofen, i.e. 1-(ethoxycarbonyl)ethyl 5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoate; on its
30 own, the active substance is conventionally employed

- 4 -

pre- and post-emergence in soya beans and cereals at
50 - 500 g of a.i./ha;

5 b3) bifenox, i.e. methyl 5-(2,4-dichlorophenoxy)-
2-nitrobenzoate; on its own, the active substance is
conventionally employed pre- and post-emergence in
cereals, rice and maize at a rate of 50 to 1000 g of
a.i./ha;

10 b4) fluoroglycofen-ethyl, i.e. ethoxycarbonylmethyl
5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitro-
benzoate; its use as a single active substance is
known pre- and post-emergence in cereals and soya
beans at a rate of 5 to 50 g of a.i./ha;

15 b5) acifluorfen, i.e. 5-[2-chloro-4-(trifluoromethyl)-
phenoxy]-2-nitrobenzoic acid or its salts, such as
the sodium salt; the single active substance is
conventionally employed pre- and post-emergence in
soya beans and cereals at 100 - 500 g of a.i./ha;
and:

20 b6) fomesafen, i.e. N-methylsulfonyl-5-[2-chloro-4-(tri-
fluoromethyl)phenoxy]-2-nitrobenzamide; its use as
a single active substance is known pre- and post-
emergence in soya beans or cereals at 50 to 1000 g
of a.i./ha.

25 The compounds b1 to b6 are described, for example, in
"The Pesticide Manual" 9th Edition, British Crop Protec-
tion Council 1991 and in the literature cited therein and
are known as protoporphyrinogen oxidase inhibitor herbi-
cides.

30 The anionic surfactant (C) is, for example, a wetting
agent from the group of the fatty alcohol polyglycol
ether sulfates and their salts, preferably of the
C₁₀-C₁₈-fatty alcohol polyglycol ether sulfates in the form
of the alkali metal salts, alkaline earth metal salts or

- 5 -

ammonium salts or the substituted ammonium salts; substituted ammonium salts are, for example, primary, secondary, tertiary and quaternary ammonium salts having substituents from the group consisting of alkyl or hydroxyalkyl, preferably having 1 to 4 carbon atoms. Sodium C₁₂-C₁₄-fatty alcohol diethylene glycol ether sulfate (®Genapol LRO, Hoechst AG) is preferably employed.

US-A-5,324,708 has already disclosed the preparation of formulations with a content of a combination of the herbicides glufosinate-ammonium, specifically in the form of a non-hygroscopic salt, and oxyfluorfen. Combinations of these herbicides with anionic wetting agents are not described in this publication. US-A-5,324,708 lacks biological examples of combinations of the herbicides as well as information on synergistically increased activities of combinations of glufosinate-ammonium and oxyfluorfen.

Research Disclosure 275 (1987), 154 discloses the combination of glufosinate-ammonium with other herbicides to widen the spectrum of action of glufosinate-ammonium. Inter alia, this publication mentions the combination of glufosinate-ammonium and oxyfluorfen for use in cotton. The publication lacks information on synergistically increased activities of the combination of glufosinate-ammonium and oxyfluorfen or combinations with fatty alcohol polyglycol ether sulfates.

Surprisingly, it has emerged that superadditive (= synergistic) effects are observed when type A herbicides are used jointly with one or more active substances from amongst group B in the presence of surfactant C. The activity in the combinations is more pronounced than in the individual herbicides employed alone in the presence of wetting agent C. These effects permit the application rate to be reduced, a broader spectrum of broad-leaved weeds and grass weeds to be controlled, more rapid onset

- 6 -

of the herbicidal action, a more prolonged action, better control of the harmful plants by only one application, or few applications, and widening of the period of time within which the product can be used. These properties
5 are required in weed control practice to keep agricultural crops free from undesirable competing plants and thus to guarantee and/or increase yield from a qualitative and quantitative point of view. These novel combinations markedly surpass the prior art with a view to the above-
10 described properties.

The best possible choice of the weight ratio and the application rates depends, for example, on the components of the mixture, the development stage of the broad-leaved weeds or grass weeds, the weed spectrum, and environmen-
15 tal and climatic factors.

The weight ratios A:B of the combined herbicides of type A and type B can therefore vary within wide limits and are, as a rule, between 100:1 and 1:5, preferably between 10:1 and 1:1. The following weight ratios A:B are
20 preferred for the combination of type A herbicides, in particular glufosinate-ammonium (racemic):

- with oxyfluorfen 10:1 to 2:1, in particular 8:1 to 3:1.
- with lactofen 10:1 to 2:1, in particular 8:1 to 3:1.
- with bifenox 10:1 to 2:1, in particular 8:1 to 3:1.
- 25 - with fluoroglycofen 100:1 to 10:1, in particular 50:1 to 10:1.
- with acifluorfen 10:1 to 2:1, in particular 8:1 to 3:1.
- with fomesafen 10:1 to 2:1, in particular 8:1 to 3:1.

The application rate of the herbicides in question, when
30 used in the form of a combination, is considerably below the application rate when applying the herbicide in question singly, while providing the same herbicidal action. As a rule, application rates of 100 to 600 g of a.i./ha type A herbicide, preferably glufosinat -ammoni-
35 um, and 50 to 150 g of a.i./ha nitrodiphenyl ethers, such as oxyfluorfen and lactofen, are preferred.

- 7 -

The optimal application rate of the anionic surfactant of type C depends on the application rate of the herbicides as well as the factors which have already been mentioned and is, as a rule, between 100 and 2000 g of surfactant per hectare, based on surface-active substance (SAS), preferably 500 to 1500 g of SAS/ha. Accordingly, the weight ratio of herbicide A to surfactant C is preferably 1:1 to 1:10, in particular 1:2 to 1:5.

The compositions according to the invention act against a broad spectrum of weeds. For example, they are suitable for controlling annual and perennial weeds such as, for example, Agropyron, Paspalum, Cynodon, Imperata, Pennisetum, Convolvulus, Cirsium, Rumex and others.

The compositions according to the invention can be used to selectively control annual and perennial harmful plants in plantation crops such as oil palm, coconut palm, India-rubber tree, citrus, pineapples, cotton, coffee, cocoa and the like, as well as in fruit production and viticulture. Equally, the combinations according to the invention can be employed in arable crop production using the no-till, or zero-till, method. Alternatively, they can be used in a non-selective manner on paths, open spaces and industrial sites and the like to keep these areas free from undesirable vegetation.

The herbicidal compositions according to the invention are distinguished by a long-term herbicidal action with a rapid onset. Rain fastness of the active substances in the combinations according to the invention is good. A particular advantage is the fact that the effective dosages of compounds of the formula (A) and (B) used in the combinations are so low that their soil action is reduced considerably. This makes their use in sensitive crops possible for the first time, and, additionally, contamination of the groundwater is virtually avoided. The combination according to the invention of active substances and wetting agents allows the required rate of

- 8 -

application of the active substances to be reduced considerably.

The invention thus also relates to a method of controlling undesirable vegetation which comprises applying one or more type A herbicides together with one or more type B herbicides and a type C anionic surfactant to the harmful plants, parts of these plants or the area under cultivation.

The active substance combinations according to the invention can either exist in the form of mixed formulations of the three components, if appropriate together with other customary formulation auxiliaries, which mixed formulations are then applied in the usual manner in the form of a dilution with water, or else they can be prepared in the form of so-called tank mixes by joint dilution with water of the components which are formulated separately, or partly separately.

The type A and type B compounds or their combinations, if appropriate together with surfactant C, can be formulated in various ways, depending on the prevailing biological and/or chemico-physical parameters. Suitable general possibilities for formulations are, for example: wettable powders (WP), emulsifiable concentrates (EC), aqueous solutions (SL), emulsions (EW) such as oil-in-water and water-in-oil emulsions, sprayable solutions or emulsions, oil- or water-based dispersions, suspoemulsions, dusts (DP), seed-dressing products, granules for soil application or for spreading, or water-dispersible granules (WG), ULV formulations, microcapsules or waxes.

The individual types of formulation are known in principle and are described, for example, in: Winnacker-Küchler, "Chemische Technologie" [Chemical Technology], Vol. 7, C. Hauser Verlag Munich, 4th Ed. 1986; van Valkenburg, "Pesticide Formulations", Marcel Dekker N.Y., 1973; K. Martens, "Spray Drying Handbook", 3rd Ed. 1979,

G. Goodwin Ltd. London.

The formulation auxiliaries required, such as inert materials, surfactants, solvents and other additives are also known and are described, for example, in: Watkins, 5 "Handbook of Insecticide Dust Diluents and Carriers", 2nd Ed., Darland Books, Caldwell N.J.; H.v. Olphen, "Introduction to Clay Colloid Chemistry"; 2nd Ed., J. Wiley & Sons, N.Y. Marsden, "Solvents Guide", 2nd Ed., Interscience, N.Y. 1950; McCutcheon's, "Detergents and 10 Emulsifiers Annual", MC Publ. Corp., Ridgewood N.J.; Sisley and Wood, "Encyclopedia of Surface Active Agents", Chem. Publ. Co. Inc., N.Y. 1964; Schönfeldt, "Grenzflächenaktive Äthylenoxidaddukte" [Surface-active ethylene oxide adducts], Wiss. Verlagsgesellschaft, 15 Stuttgart 1976, Winnacker-Küchler, "Chemische Technologie" [Chemical Technology], Vol. 7, C. Hauser Verlag Munich, 4th Ed. 1986.

Based on these formulations, it is also possible to prepare combinations with other pesticidally active 20 substances, such as other herbicides, fungicides or insecticides, and also safeners, fertilizers and/or growth regulators, for example in the form of a ready mix or a tank mix.

Wettable powders are preparations which are uniformly 25 dispersible in water and which, besides the active substance, also comprise ionic or nonionic surfactants (wetting agents, dispersants), for example polyoxyethylated alkylphenols, polyethoxylated fatty alcohols or fatty amines, alkanesulfonates or alkylbenzenesulfonates, 30 sodium lignosulfonate, sodium 2,2'-dinaphthylmethane-6,6'-disulfonate, sodium dibutyl-naphthalenesulfonate or else sodium oleoylmethyltaurate, in addition to a diluent or inert substance.

Emulsifiable concentrates are prepared by dissolving the 35 active substance in an organic solvent, for example

- 10 -

butanol, cyclohexanone, dimethylformamide, xylene or else higher-boiling aromatics or hydrocarbons, with the addition of one or more ionic or nonionic surfactants (emulsifiers). Examples of emulsifiers which can be used
5 are: calcium alkylarylsulfonates, such as calcium dodecylbenzenesulfonate, or nonionic emulsifiers, such as fatty acid polyglycol esters, alkylaryl polyglycol ethers, fatty alcohol polyglycol ethers, propylene oxide/ethylene oxide condensates, alkyl polyethers,
10 sorbitan fatty acid esters, polyoxyethylene sorbitan fatty acid esters or polyoxyethylene sorbitol esters.

Dusts are obtained by grinding the active substance with finely divided solid materials, for example talc, natural clays, such as kaolin, bentonite and pyrophyllite, or
15 diatomaceous earth.

Granules can be prepared either by spraying the active substance onto adsorptive, granulated inert material, or by applying active substance concentrates to the surface of carriers, such as sand, kaolinite or granulated inert
20 material, with the aid of binders, for example polyvinyl alcohol, sodium polyacrylate or else mineral oils. Suitable active substances can also be granulated in the manner customary for the preparation of fertilizer granules, if desired as a mixture with fertilizers.
25 Water-dispersible granules are, as a rule, prepared by processes such as spray-drying, fluidized-bed granulation, disc granulation, mixing using high-speed mixers, and extrusion without solid inert material.

As a rule, the agrochemical preparations comprise 0.1 to
30 99 percent by weight, in particular 2 to 95% by weight, of active substances of types A and/or B, the following concentrations being customary, depending on the type of formulation:

In wettable powders, the active substance concentration
35 is, for example, approximately 10 to 95% by weight, the

- 11 -

remainder to 100% by weight being composed of customary formulation components. In the case of emulsifiable concentrates, the active substance concentration can be, for example, 5 to 80% by weight.

- 5 As a rule, formulations in the form of dusts comprise 5 to 20% by weight of active substance, sprayable solutions approximately 0.2 to 25% by weight of active substance. In the case of granules, such as dispersible granules, the active substance content depends partly on whether
10 the active compound is in liquid or solid form and on which granulation auxiliaries and fillers are used. As a rule, the content in the water-dispersible granules amounts to between 10 and 90% by weight.

- In addition, the active substance formulations mentioned
15 comprise, if appropriate, the adhesives, wetting agents, dispersants, emulsifiers, preservatives, antifreeze agents, solvents, fillers, colorants, carriers, anti-foams, evaporation inhibitors and pH or viscosity regulators which are customary in each case.

- 20 For use, the formulations, which are in commercially available form, are, if appropriate, diluted in the customary manner, for example using water in the case of wettable powders, emulsifiable concentrates, dispersions and water-dispersible granules. Preparations in the form
25 of dusts, soil granules, granules for spreading and sprayable solutions are conventionally not diluted any further with other inert substances prior to use.

- The active substances can be applied to the plants, parts of the plants, seeds of the plants or the area under
30 cultivation (tilled soil), preferably to the green plants and parts of the plants and, if desired, additionally to the tilled soil.

- A possible use is the joint application of the active substances in the form of tank mixtures, where the concentrated formulations of the individual active substances,
35

- 12 -

in the form of their optimal formulations, are mixed jointly with water in the tank, and the spray mixture obtained is applied.

A joint herbicidal formulation of the combination of active substances A and B and surfactant C according to the invention has the advantage that it can be applied more easily because the amounts of the components have already been adjusted to the correct ratio. Moreover, the auxiliaries of the formulation can be selected to suit each other in the best possible way, while a tank mix of various formulations may result in undesirable combinations of auxiliaries. However, most types of formulation are not suitable for a joint formulation because components A, B and C have different physical properties. Type A active substances and surfactant C are hydrophilic and are conventionally formulated as an aqueous solution comprising a large amount of salt. In contrast, active substances B are largely insoluble in water and are conventionally formulated as emulsifiable concentrates or granules. The joint formulation of the type of the abovementioned individual formulations is not possible without problems. Attempts to achieve joint formulation as emulsifiable suspensions, dispersions or emulsions are usually unsuccessful and are limited with regard to stability and desirable use characteristics.

The invention therefore also provides a specific mixed formulation which does not have the abovementioned disadvantages, and its use. The mixed formulation is an oil-in-water emulsion (EW) which comprises

- a) 1 to 15% by weight of active substance of the abovementioned type A (glufosinate-ammonium or analogous active substance),
- b) 0.1 to 5% by weight of active substance of the abovementioned type B (nitrodiphenyl ether),
- c) 1-15% by weight of anionic surfactant from the

- 13 -

group of the fatty alcohol polyglycol ether sulfates,

- d) 3 to 30% by weight, preferably 3-20% by weight, in particular 3-15% by weight, of organic solvent,
- e) 40 to 60% by weight of water,
- f) 2 to 10% by weight of emulsifier or emulsifier mixture and
- g) 0 to 20% by weight of customary formulation auxiliaries.

Suitable solvents are, for example, nonpolar solvents, polar protic or aprotic dipolar solvents and mixtures of these, the organic solvent together with the nitrodiphenyl ether herbicide forming an emulsified organic phase next to the aqueous phase, which comprises the type A herbicide.

Examples of suitable solvents are:

- aliphatic and aromatic hydrocarbons, such as, for example, mineral oils or toluene, xylenes and naphthalene derivatives;
- halogenated aliphatic and aromatic hydrocarbons, such as methylene chloride or chlorobenzene;
- ethers, such as diethyl ether, tetrahydrofuran (THF), dioxane, alkylene glycol monoalkyl ethers and alkylene glycol dialkyl ethers, such as, for example, propylene glycol monomethyl ether, propylene glycol monoethyl ether, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, diglyme and tetraglyme;
- amides, such as dimethylformamide (DMF), dimethylacetamide and N-methylpyrrolidone;
- ketones, such as acetone and cyclohexanone;
- nitriles, such as acetonitrile, propionitrile, butyronitrile and benzonitrile;
- sulfoxides and sulfones, such as dimethyl sulfoxide (DMSO) and sulfolane;
- oils, for example vegetable-based oils, such as

- 14 -

maize germ oil and rapeseed oil.

Alcohols, such as the alkanols methanol, ethanol, n- and i-propanol or n-, i-, t- and 2-butanol, can also frequently be employed, especially in combinations of solvents. Preferred organic solvents are aromatic hydrocarbons, such as, for example, toluene, xylenes and naphthalene derivatives.

Suitable emulsifiers are ionic surfactants and nonionic surfactants, the following being suitable ionic emulsifiers:

calcium alkylarylsulfonates, such as calcium dodecylbenzenesulfonate, phosphated propylene oxide/ethylene oxide condensates, such as phosphated PO/EO block copolymers or phosphated tristyrylphenol polyglycol ethers; and examples of nonionic emulsifiers being: fatty acid polyglycol esters, alkylaryl polyglycol ethers, fatty alcohol polyglycol ethers, propylene oxide/ethylene oxide condensates, such as PO/EO block copolymers, alkyl polyethers, polyols, such as polyvinyl alcohol, sorbitan fatty acid esters, polyoxyethylene sorbitan fatty acid esters or polyoxyethylene sorbitol esters.

Preferably suitable are emulsifier mixtures of modified polyvinyl alcohol (for example [®]Mowiol 3/83, [®]Mowiol 4/88; Hoechst), phosphated PO/EO block copolymers (for example Hoe S 3618, Hoechst), calcium dodecylbenzenesulfonate and fatty alcohol polyglycol ether.

Customary formulation auxiliaries (g) are, for example, the customary formulation auxiliaries which have already been mentioned above in general terms; preferred auxiliaries are

- antifreeze agents and evaporation inhibitors, such as glycerol, for example in an amount of 2 to 10% by weight,
- 35 - preservatives, for example [®]Mergal K9N (Ri del) or [®]Cobate C, at the concentrations at which the compo-

- 15 -

sitions employed specifically in each case are conventionally used,

antifoams, for example silicone antifoam, such as antifoam emulsion SRE, at the customary use concentrations.

Preferred mixed formulations are EW formulations which comprise

- a) 5 to 12% by weight of glufosinate-ammonium,
- b) 1 to 4% by weight of nitrodiphenyl ether,
- 10 c) 5 to 12% by weight of fatty alcohol polyglycol ether sulfate,
- d) 3 to 20% by weight, preferably 3-15% by weight, in particular 5 to 10% by weight, of organic solvent,
- 15 e) 45 to 55% by weight of water,
- f) 4 to 8% by weight of emulsifier or emulsifier mixture, and
- g) 0 to 10% by weight of customary formulation auxiliaries.

- 20 Preferred mixed formulations are those which comprise 6 to 18% by weight of a herbicide combination of glufosinate-ammonium (racemic) and oxyfluorfen or lactofen in a weight ratio A:B of 10:1 to 2:1 and 5 to 12% by weight of sodium C₁₂-C₁₄-fatty alcohol diethylene glycol ether sulfate as anionic surfactant C in a weight ratio of herbicide A : wetting agent C of 1:1 to 1:10.

The EW mixed formulations are distinguished by good physical and chemical storage stability. The formulations can be handled more easily than a tank mix. Use of the mixed formulations gives biological results which are not only equal to the results obtained with a tank mix from the separately formulated components, but, as a rule, are even better.

A. General formulation examples:

- 35 a) A dust is obtained by mixing 10 parts by weight of

- 16 -

an active substance combination according to the invention and 90 parts by weight of talc as inert substance and comminuting the mixture in a hammer mill.

- 5 b) A wettable powder which is readily dispersible in water is obtained by mixing 25 parts by weight of active substances A + B, 64 parts by weight of kaolin-containing quartz as inert substance, 10 parts by weight of potassium lignosulfonate and 1
10 part by weight of sodium oleoylmethyltaurinate as wetting agent and dispersant, and grinding the mixture in a pinned-disk mill.
- c) A dispersion concentrate which is readily dispersible in water is obtained by mixing 20 parts by
15 weight of active substances A + B with 6 parts by weight of alkylphenol polyglycol ether ([®]Triton X 207), 3 parts by weight of isotridecanol polyglycol ether (8 EO) and 71 parts by weight of paraffinic mineral oil (boiling range for example approximately 255 to 277°C) and grinding the mixture in a
20 ball mill to a fineness of below 5 microns.
- d) An emulsifiable concentrate is obtained from 15 parts by weight of cyclohexanone as the solvent and 10 parts by weight of oxethylated nonylphenol as the
25 emulsifier.
- e) Water-dispersible granules are obtained by mixing 75 parts by weight of active substances A + B, 10 parts by weight of calcium lignosulfonate, 5 parts by weight of sodium lauryl sulfate,
30 3 parts by weight of polyvinyl alcohol and 7 parts by weight of kaolin, grinding the mixture in a pinned-disk mill and granulating the powder in a fluidized bed by spraying on water as granulation liquid.

- 17 -

- f) Water-dispersible granules are also obtained by homogenizing and precomminuting, in a colloid mill, 25 parts by weight of active substances A + B, 5 parts by weight of sodium 2,2'-dinaphthylmethane-6,6'-disulfonate, 2 parts by weight of sodium oleoylmethyltaurate, 1 part by weight of polyvinyl alcohol, 17 parts by weight of calcium carbonate and 50 parts by weight of water, subsequently grinding the mixture in a bead mill and atomizing and drying the resulting suspension in a spray tower by means of a single-substance nozzle.

B. Formulation examples of emulsions (EW)

- B1. EW formulation comprising 10% of glufosinate-ammonium, 3.3% of oxyfluorfen and 10% of fatty alcohol polyglycol ether sulfate

- A solution of 3.47% by weight of oxyfluorfen 95% pure (= 3.3% of a.i.), 1.00% by weight of Hoe S 3618, 2.00% by weight of phenylsulfonate CA, 1.30% by weight of antifoam emulsion SRE, 0.25% by weight of ®Arlypon F and 7.88% by weight of ®Solvesso 200 is run slowly at 20°C with stirring into an aqueous solution of 10.00% by weight of glufosinate-ammonium, 14.29% by weight of ®Genapol LRO paste (70% pure = 10% of surface-active substance), 0.75% by weight of ®Mowiol 3/83, 1.00% by weight of ®Mowiol 4/88, 0.20% by weight of ®Mergal K9N, 1.50% by weight of propylene glycol monomethyl ether, 5.50% by weight of glycerol and 50.86% by weight of water

- 18 -

and stirring of the mixture is continued for one hour. The emulsion formed is physically and chemically stable at between -10°C and +50°C.

- 5 B2. EW formulation comprising 9.5% of glufosinate-ammonium, 1.95% of oxyfluorfen and 10% of fatty alcohol polyglycol ether sulfate

A solution of

- 2.00% by weight of oxyfluorfen 95% pure (= 1.95% of a.i.),
10 1.00% by weight of Hoe S 3618,
2.00% by weight of Phenylsulfonate CA,
1.30% by weight of antifoam emulsion SRE,
0.25% by weight of ®Arlypon F and
9.02% by weight of ®Solvesso 200
15 is run slowly at 20°C with stirring into an aqueous solution of
9.50% by weight of glufosinate-ammonium,
14.29% by weight of ®Genapol LRO paste (70% pure = 10% of surface-active substance),
20 0.20% by weight of ®Mergal K9N,
1.50% by weight of propylene glycol monomethyl ether,
5.50% by weight of glycerol and
53.44% by weight of water

- 25 and stirring of the mixture is continued for one hour. The emulsion formed is physically and chemically stable at between -10°C and +40°C.

- B3. EW formulation comprising 10% of glufosinate-ammonium, 2% of oxyfluorfen and 10% of fatty alcohol polyglycol ether sulfate
30

A solution of

- 2.05% by weight of oxyfluorfen 94% pure (= 2.0% of a.i.),
16.00% by weight of ®Solvesso 200,

- 19 -

2.00% by weight of Phenylsulfonate CA and
0.25% by weight of ®Arlypon F
is run slowly at 20°C with stirring into an aqueous
solution of
5 10.00% by weight of glufosinate-ammonium,
34.50% by weight of ®Genapol LRO paste (28%
pure = 9.66% of surface-active substance),
0.20% by weight of ®Mergal K9N,
4.00% by weight of glycerol,
10 4.88% by weight of Hoe S 3618 sodium salt (20.8%
pure),
1.21% by weight of antifoam emulsion SRE and
24.91% by weight of water
and stirring of the mixture is continued for one
15 hour. The emulsion formed is physically and chemi-
cally stable at between -10°C and +50°C.

B4. EW formulation comprising 10% of glufosinate-ammoni-
um, 2% of oxyfluorfen and 10% of fatty alcohol
polyglycol ether sulfate

20 A solution of
2.05% by weight of oxyfluorfen 94% pure (= 2.0% of
a.i.),
10.00% by weight of ®Solvesso 200,
6.00% by weight of cyclohexanone,
25 2.00% by weight of Phenylsulfonate CA and
0.25% by weight of ®Arlypon F
is run slowly at 20°C with stirring into an aqueous
solution of
10.00% by weight of glufosinate-ammonium,
30 34.50% by weight of ®Genapol LRO paste (28%
pure = 9.66% of surface-active sub-
stance),
0.20% by weight of ®Mergal K9N,
4.00% by weight of glycerol,
35 4.88% by weight of Hoe S 3618 sodium salt (20.8%
pure),
1.21% by weight of antifoam emulsion SRE and

- 20 -

24.91% by weight of water
and stirring of the mixture is continued for one
hour. The emulsion formed is physically and chemi-
cally stable at between -10°C and +40°C.

- 5 B5. EW formulation comprising 14% of glufosinate-ammoni-
um, 2.8% of oxyfluorfen and 10% of fatty alcohol
polyglycol ether sulfate

A solution of

10 2.89% by weight of oxyfluorfen 94% pure (= 2.0% of
a.i.),

15.00% by weight of ®Solvesso 200,

2.00% by weight of Phenylsulfonate CA and

0.25% by weight of ®Arlypon F

15 is run slowly at 20°C with stirring into an aqueous
solution of

14.00% by weight of glufosinate-ammonium,

34.50% by weight of ®Genapol LRO paste (28%
pure = 9.66% of surface-active substance),

0.20% by weight of ®Mergal K9N,

20 4.00% by weight of glycerol,

9.76% by weight of Hoe S 3618 sodium salt (20.8%
pure),

1.21% by weight of antifoam emulsion SRE and

16.14% by weight of water

25 and stirring of the mixture is continued for one
hour. The emulsion formed is physically and chemi-
cally stable at between -10°C and +40°C.

Explanations/abbreviations regarding Examples B1 and B5:

®Genapol LRC (Hoechst):

30 Sodium C₁₂-C₁₄-fatty alcohol diethylene glycol ether
sulfate,

®Mowiol 3/83 (Hoechst):

Polyvinyl alcohol, prepared by partial hydrolysis of
polyvinyl acetate, with a viscosity of 3 cP, mea-

- 21 -

sured in a 4% strength aqueous solution at 20°C, and a degree of hydrolysis of 83 mole perc nt.

®Mcwio1 4/88 (Hoechst):

5 Polyvinyl alcohol, prepared by partial hydrolysis of polyvinyl acetate, with a viscosity of 4 cP, measured in a 4% strength aqueous solution at 20°C, and a degree of hydrolysis of 88 mole percent.

Hoe S 3618 (Hoechst):

Bis-monophosphoric ester of a PO/EO block copolymer

10	Phenylsulfonate CA (Hoechst):	Calcium C ₁₂ -alkyl- benzenesulfonate
	®Mergal K9N (Riedel de Haen):	Isothiazolinone mixture
	®Arlypon F (Hoechst):	C ₁₂ -C ₁₄ -fatty alcohol ethoxylate (2.5 EO)
15	®Solvesso 200 (ESSO):	aromatic solvent
	Antifoam emulsion SRE (Wacker):	Silicone-oil-based antifoam

Biological Examples

20 A range of economically important broad-leaved weeds and grass weeds are grown under natural field conditions. After certain development stages (expressed by the number of unfolded leaves or the plant height) have been reached, a tank mix of the herbicides in question together with surfactant C, or a tank mix of the herbicide mix-

25 tures and the surfactant C, are applied under standard conditions, i.e. using a plot sprayer and 300-400 liters of water per hectare.

30 In the interval of 1 to 3 weeks after application, the herbicidal activity of the active substances, or active substance mixtures, is scored visually by assessing the treated plots in comparison to the untreated control plots. Damage to, and development of, all aerial parts of the plants are recorded.

- 22 -

In most cases, the synergistically increased action is so high that the action of the combination considerably surpasses the formal (calculated) total of the actions of the individual substances. Such a greatly increased action was not to be expected based on the known actions of the individual active substances. Particular mention must be made of the fact that, when assessing synergism between the active substances employed, the highly different application rates of the individual active substances must be borne in mind. Thus, it is not expedient to compare the actions of the active substance combinations and the individual active substances in each case at identical rates of application. The amounts of active substance to be dispensed with according to the invention can only be seen from the superadditive increase in action when using the combined application rates or by the reduction in the application rates of the two individual active substances in the combination in comparison to the individual active substances while the action remains the same in each case. A further advantage of the active substance combinations can be seen from more rapid onset of the action, or a longer-term action, in a broad range of economically relevant harmful plants. Some biological results are listed in Tables 1 to 3.

Table 1: Herbicidal action (for abbreviations, see after Table 3)

	Dosage [g of a.i./ha or g of SAS/ha]	Herbicidal action in % after		Harmful plant
		14 days	28 days	
A1 + C1	450 + 450	76.0	45.5	Mix
B1 + C1	90 + 450	15.0	3.7	"
A1 + B1 + C1	450 + 90 + 450	86.8	55.0	"
A1 + C1	450 + 450	60.0	10.0	GERSP
B1 + C1	90 + 450	12.5	22.5	"
A1 + B1 + C1	450 + 90 + 450	72.5	55.0	"
A1 + C1	450 + 450	60.0	10.0	GERSP
B2 + C1	90 + 450	40.0	7.5	"
A1 + B2 + C1	450 + 90 + 450	90.0	42.5	"

Table 2: Herbicidal action (for abbreviations, see after Table 3)

	Dosage [g of a.i./ha or g of SAS/ha]	Herbicidal action in % after		Harmful plant
		7 days	28 days	
A1 + C1	450 + 450	50	6	SONAS
B1 + C1	90 + 450	15	4	"
A1 + B1 + C1	450 + 90 + 450	85	40	"
A1 + C1	450 + 450	50	6	SONAS
B2 + C1	90 + 450	6	5	"
A1 + B2 + C1	450 + 90 + 450	85	20	"
A1 + C1	450 + 450	48	18	CONAR
B1 + C1	90 + 450	56	4	"
A1 + B1 + C1	450 + 90 + 450	97	28	"

Table 3: Herbicidal action

	Dosage [g of a.i./ha or g of SAS/ha]	Herbicidal action in % after		Harmful plant	
		7 days	14 days		
5	A1 + C1	450 + 450	49	51	CONAR
	B2 + C1	90 + 450	6	26	"
	A1 + B2 + C1	450 + 90 + 450	93	80	"
5	A1 + C1	450 + 450	13	88	ERISP
	B2 + C1	90 + 450	3	29	"
	A1 + B2 + C1	450 + 90 + 450	75	93	"
10	A1 + C1	450 + 450	13	88	ERISP
	B2 + C1	90 + 450	1	21	"
	A1 + B2 + C1	450 + 90 + 450	75	95	"
10	A1 + C1	450 + 450	48	18	CONAR
	B1 + C1	90 + 450	56	4	"
	A1 + B1 + C1	450 + 90 + 450	97	28	"

Abbreviations in Tables 1 to 3:

15	A1	=	Glufosinate-ammonium (rac.)
	B1	=	Oxyfluorfen
	B2	=	Lactofen
	C1	=	Sodium C ₁₂ /C ₁₄ -fatty alcohol diethylene glycol ether sulfate (®Genapol LRO)
20	CONAR	=	Convolvulus arvensis
	ERISP	=	Erigeron sp.
	GERSP	=	Geranium sp.
	SONAS	=	Sonchus asper
	Mix	=	Mixture of harmful plants: CONAR, ERISP, GERSP, SONAS
25	a.i.	=	Based on pure herbicidal active substance
	SAS	=	Based on pure surfactant (= wash-active substance)
	-	=	Not tested

WO 96/22692

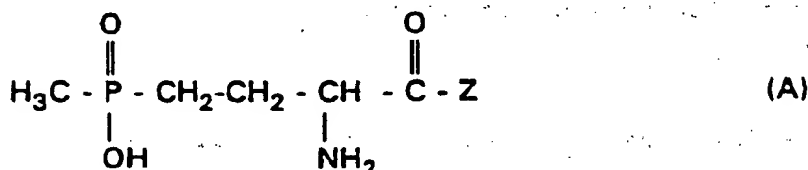
- 25 -

PCT/EP96/00072

Patent claims

1. A herbicidal composition which comprises an effective content of a combination of

5 A) one or more compounds of the formula (A) or salts thereof



where

10 Z is a radical of the formula -OM, -NHCH(CH₃)CONHCH(CH₃)COOM or -NHCH(CH₃)CONHCH[CH₂CH(CH₃)₂]COOM in which M is in each case hydrogen or an inorganic or organic cation,

15 B) one or more compounds of the group of the nitro-diphenyl ether herbicides and
C) an anionic surfactant from the series of the alkyl polyglycol ether sulfates.

2. A herbicidal composition as claimed in claim 1, which comprises

20 A) a herbicide from the group consisting of D,L-glufosinate, D,L-glufosinate-ammonium, L-glufosinate, L-glufosinate-ammonium, bialaphos and bialaphos-sodium,
B) a nitrodiphenyl ether herbicide from the group consisting of oxyfluorfen, lactofen, bifenox, fluoroglycofen-ethyl, acifluorfen and fomesafen and
25 C) an anionic wetting agent from the group of the C₁₀-C₁₈-fatty alcohol polyglycol ether sulfates in the form of the alkali metal salts, alkaline earth metal salts or ammonium salts or the substituted ammonium salts.

30 3. A herbicidal composition as claimed in claim 1 or 2, wherein the weight ratios A:B of the combined herbi-

- 26 -

cides of type A and type B are between 100:1 and 1:5.

4. A herbicidal composition as claimed in any of claims 1 to 3, wherein the weight ratio A:B of
 - 5 A) glufosinate-ammonium (racemic) and
 - B) oxyfluorfen or lactofenis 10:1 to 2:1.
5. A herbicidal composition as claimed in claim 4, wherein the weight ratio A:B is from 8:1 to 3:1.
- 10 6. A herbicidal composition as claimed in any of claims 1 to 5, wherein the weight ratio of herbicide A to wetting agent C is 1:1 to 1:10.
- 15 7. A method of controlling undesirable vegetation, which comprises applying one or more type A herbicides with one or more type B herbicides and a type C anionic wetting agent to the harmful plants, parts of these plants or the area under cultivation, types A, B and C being as defined in any of claims 1 to 6.
- 20 8. The use of a combination of
 - a) one or more type A herbicides,
 - b) one or more type B herbicides and
 - c) a type C anionic wetting agentas a herbicidal composition for controlling undesirable vegetation, types A, B and C being as defined in any of
- 25 claims 1 to 6.
9. A herbicidal formulation based on aqueous emulsions (EW), which comprises
 - a) 1 to 15% by weight of a herbicidally active substance of type A,
 - 30 b) 0.1 to 5% by weight of herbicidally active substance of type B,
 - c) 1-15% by weight of anionic surfactant of type C,
 - d) 3 to 30% by weight of organic solvent,

- 27 -

- e) 40 to 60% by weight of water,
f) 2 to 10% by weight of emulsifier or emulsifier mixture and
g) 0 to 20% by weight of customary formulation auxiliaries,
5 types A), B) and C) in components a), b) and c) being as defined in claim 1.
10. A herbicidal formulation as claimed in claim 9, which comprises
10 a) 5 to 12% by weight of glufosinate-ammonium,
b) 1 to 4% by weight of nitrodiphenyl ether,
c) 5 to 12% by weight of fatty alcohol polyglycol ether sulfate,
d) 3 to 20% by weight of organic solvent,
15 e) 45 to 55% by weight of water,
f) 4 to 8% by weight of emulsifier or emulsifier mixture, and
g) 0 to 10% by weight of customary formulation auxiliaries.
- 20 11. A herbicidal formulation as claimed in claim 9 or 10, which comprises
6 to 18% by weight of a herbicide combination of glufosinate-ammonium (racemic) and oxyfluorfen or lactofen in a weight ratio A:B of 10:1 to
25 2:1 and
5 to 12% by weight of sodium C₁₂-C₁₄-fatty alcohol diethylene glycol ether sulfate as anionic surfactant C in a weight ratio herbicide A : wetting agent C of 1:1 to 1:10.

Fetherstonburgh & Co.,
Ottawa, Canada
Patent Agents

95/M 200 WO

- 28 -

Abstract

Synergistic herbicidal compositions based on glufosinate and nitrodiphenyl ethers, and their formulations

Herbicidal compositions comprising

- A) glufosinate or its salts or analogous agents such as bialaphos,
- B) a nitrodiphenyl ether herbicide such as oxyfluorfen and
- C) an alkyl polyglycol ether sulfate surfactant

have synergistic herbicidal activities.

The joint formulation of components A, B and C is possible in the form of an aqueous emulsion which comprises 1-15% of A), 0.1 to 5% of B), 1-15% of C), 3 to 30% of organic solvent, 40-60% of water, 2-10% of emulsifier and 0 to 20% of customary formulation auxiliaries.

1. The first part of the document is a list of the names of the persons who have been named in the document. The names are listed in alphabetical order.

2. The second part of the document is a list of the names of the persons who have been named in the document. The names are listed in alphabetical order.

3. The third part of the document is a list of the names of the persons who have been named in the document. The names are listed in alphabetical order.

4. The fourth part of the document is a list of the names of the persons who have been named in the document. The names are listed in alphabetical order.

5. The fifth part of the document is a list of the names of the persons who have been named in the document. The names are listed in alphabetical order.

6. The sixth part of the document is a list of the names of the persons who have been named in the document. The names are listed in alphabetical order.

7. The seventh part of the document is a list of the names of the persons who have been named in the document. The names are listed in alphabetical order.

8. The eighth part of the document is a list of the names of the persons who have been named in the document. The names are listed in alphabetical order.

9. The ninth part of the document is a list of the names of the persons who have been named in the document. The names are listed in alphabetical order.

10. The tenth part of the document is a list of the names of the persons who have been named in the document. The names are listed in alphabetical order.

11. The eleventh part of the document is a list of the names of the persons who have been named in the document. The names are listed in alphabetical order.

THIS PAGE BLANK (USPTO)